NASA TT F-11,200

RESEARCH ON THE DERIVATIVES OF PYROMELLITIC AND CUMYLIC ACIDS

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Translation of "Recherches sur les dérivés des acides cumidiniques et pyromellithique".
Helvetica Chimica Acta, Vol.8, pp.546-557, 1925.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546 AUGUST 1967

RESEARCH ON THE DERIVATIVES OF PYROMELLITIC AND CUMYLIC ACIDS

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ABSTRACT. Preparation and identification of the derivatives of cumidinic and pyromellitic acids, including analogs of phthalide and phthalimide, are discussed. As starting product, isomeric cumidinic acids, prepared from dibromoxylenes, were used instead of the conventional pyromellitic acids. Formulas and preparative methods are described, with yields for the various derivatives. Preliminary results were obtained by introduction of one and two bromine atoms into each methyl group, yielding a series of isomeric derivatives (which are given).

For the past several years, pyromellitic acid has gained some importance in scientific work. The synthesis of linear dinaphthanthracene diquinone and its derivatives, obtained by Philippi (Ref.1) or by one of us (Ref.2) from this acid, and the study of various imides of pyromellitic acid by H.Meyer and K.Steiner (Ref.3) are proof of this. However, until today, the difficulty in preparing pyromellitic acid constituted an obstacle to a more detailed study of its reactions. Philippi (Ref.4) and one of us (Ref.5) indicated a synthesis of this acid, but this was by far outstripped by the method developed by J.v.Braun and G.Lemke (Ref.6) which consisted in oxidizing octohydroanthracene by means of potassium permanganate, first in alkaline and then in acid solution. It can be stated at present that pyromellitic acid is a starting product which is readily procurable.

However, v.Braun was entirely justified in warning chemists from attempting to apply to pyromellitic anhydride all of the widely differing reactions of phthalic anhydrides. In fact, Ephraim (Ref.7) found that the ethyl ether of pyromellitic acid condenses with acetic ester, just as is the case for the ether of phthalic acid, which yields a derivative of diketohydrindene. However, whereas in the second case it is possible to obtain diketohydrindene by elimination of the alcohol and the carboxylic acid, this reaction will not take place in the series of pyromellitic acid, and nothing but decomposition products are obtained.

Similarly, Silberrad (Ref.8), in applying the synthesis of fluorescein to pyromellitic anhydride, was able to produce condensation only on one end and obtained a fluorescein containing two more carboxyls than ordinary fluorescein.

However, if it is assumed that the two pairs of carboxylic groups of pyromellitic acids react each like phthalic acid, there is still one more difficulty to overcome. Any reaction of pyromellitic anhydride, even the reaction similar

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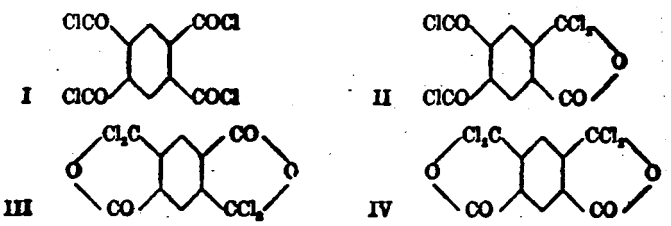
* Numbers in the margin indicate pagination in the foreign text.

to a phthalic anhydride reaction, generally gives rise to two isomers. Thus, /547
by condensation of the pyromellitic anhydride with benzene in the presence of aluminum chloride, two isomeric acids a) and b) are obtained:

This isomerism is encountered also in all asymmetric derivatives of pyromellitic acid. According to E.Ott (Ref.9), phthalic acid chloride can exist in two modifications c) and d):

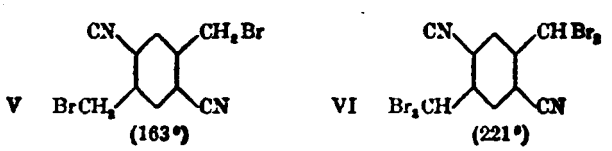
Following the same reasoning, pyromellitic chloride could theoretically exist in four modifications I - IV:



Disregarding for the moment formulas I and II, it is obvious that formulas III and IV may give rise to an entire series of isomeric derivatives, e.g., analogous to phthalide, phthalimide, etc.

The preparation and identification of the derivatives of this type is the purpose of our paper. For this, we do not start from pyromellitic acid but from isomeric cumidinic acids, for which one of us (Ref.10) described a relatively simple preparation starting from dibromoxylenes.

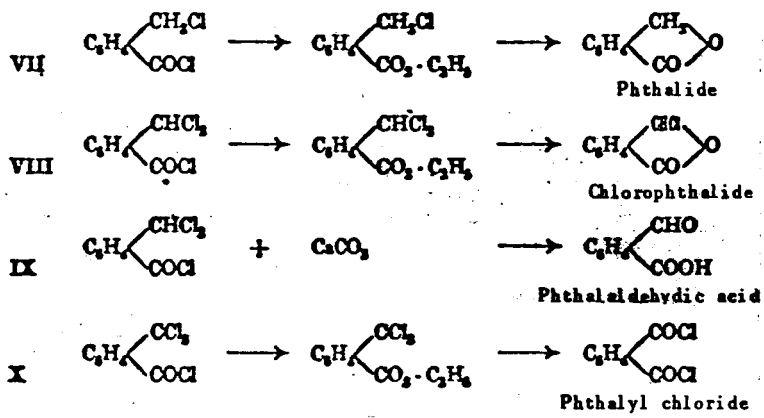
On passing a stream of bromine (preferably, bromine vapors entrained by a carboxylic anhydride stream) at a temperature of 160 - 200°C into the dinitrile of previously melted β-cumidinic acid, one obtains - depending on the duration of the process and on the temperature - either 2,5-dicyano-1,4-bis(dibromomethyl)benzene V (M.P. 163°C) or 2,5-dicyano-1,4-bis(dibromomethyl)benzene VI (M.P. 221°C):



Treating the dinitrile of α-cumidinic acid in the same manner, we obtain /548

4,6-dicyano-1,3-bis(bromomethyl)benzene (M.P. 114°C); however, if bromine atoms are to be introduced while raising the temperature, decomposition occurs and it becomes impossible to isolate the tetrabrominated product.

Instead of using nitriles as starting material, cumidinic acids can be used. W.Davies and H.Perkin (Ref.11) studied the action of halogens on toluic chlorides. They were successful in replacing, in the methyl group of o-toluic acid (the only one of interest here by analogy), 1, 2, or 3 hydrogen atoms by halogen. It should be mentioned that, if bromine is used, the chloride will first be converted into the bromide. Davies and Perkin, using this method, made the following syntheses:



Applying these processes to cumidinic acids, we were able - for the time being - to introduce 1 and 2 bromine atoms into each methyl group and to produce the reactions VII and IX, reserving a study of the two other reactions for later.

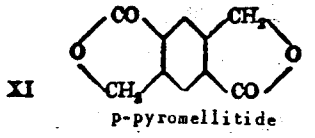
The bromination of cumidinic chlorides offers no difficulty. As mentioned before, a replacement of the chlorine by bromine takes place, followed by bromination of the secondary chain. Depending on the temperature and the amount of bromine, the final product for β-cumidinic acid will be the dibromide of 1,4-bis(bromomethyl)benzene-dicarboxylic acid (M.P. 117.5°C) or the dibromide of 1,4-bis(dibromomethyl)benzene-2,5-dicarboxylic acid (M.P. 149°C). For α-cumidinic acid, the reaction is somewhat different. In opposition to what takes place for the corresponding dinitrile, two bromine atoms are readily substituted in each methyl group, yielding - as the main product - the dibromide of 1,3-bis (dibromomethyl)benzene-4,6-dicarboxylic acid (M.P. 104°C).

The corresponding bromide of the dibrominated acid was obtained only in /549
the impure state by brominating at a temperature of about 130°C and interrupting the halogen addition rather long before the theoretical amount could have been reached. Nevertheless, this impure product was useful for the scheduled syntheses.

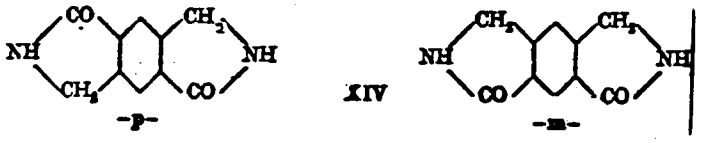
By means of these various brominated products, we were able to prepare the following isomeric derivatives:

A) Analogs of phthalides, namely the dilactone of 1,4-bis(oxymethyl)benzene-2,5-dicarboxylic acid XI and the dilactone of 1,3-bis(oxymethyl)benzene-4,6-di-

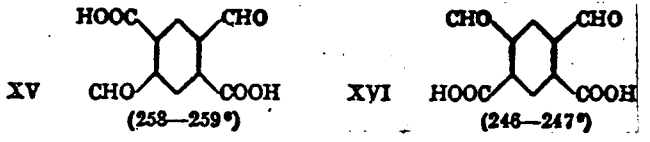
carboxylic acid XII. For simplification, we will call this p- and m-pyromellitide:



B) Analogs of phthalimidine, namely the dianhydride of 1,4-bis(aminomethyl) benzene-2,5-dicarboxylic acid XIII (p-pyromellitic diimidine) and the dianhydride of 1,3-bis(aminomethyl)benzene-4,6-dicarboxylic acid XIV (m-pyromellitic diimidine):



C) Analogs of phthalaldehydic acid, namely 1,4-dialdehydobenzene-2,5-dicarboxylic acid XV (M.P. 258 - 259°C) and 1,3-dialdehydobenzene-4,6-dicarboxylic acid XVI (M.P. 246 - 247°C):



Of all these derivatives, only the dialdehydodicarboxylic acids are useful for subsequent study. The pyromellitides and the diimidines, because of their poor solubility even in solvents of high boiling points, do not give the reactions characteristic for phthalide or for phthalimidine.

1. Preparation of Pyromellitides

Three different means can be employed here:

Heating the dibrominated dinitriles in a sealed tube at 150°C, with a solution of hydrochloric gas in 75% acetic acid (Ref.12) or, in a simpler process, saponifying the dinitriles with 70% boiling sulfuric acid:

$$C_6H_2(CH_2Br)_2(CN)_2 + 4H_2O = C_6H_2(C_2H_3O_2)_2 + 2NH_4Br.$$

Heating the ethyl esters of the dibromocumidinic acids above their melting point (Davies and Perkin analogy, loc. cit.): /550

$$C_6H_2(CH_2Br)_2(CO_2 \cdot C_2H_5)_2 = C_6H_2(C_2H_3O_2)_2 + 2C_2H_5Br.$$

Dissolving the dibromocumidinic acids in sodium carbonate; after a few minutes, the wanted product will precipitate out* (Footnote next page)

$$C_6H_2(CH_2Br)_2(CO_2Na)_2 = C_6H_2(C_2H_2O_2)_2 + 2NaBr.$$

2. Pyromellitic Diimidines

Here, ethyl ethers of dibromocumidinic acids are preferably used, passing a stream of gaseous ammonia into their boiling alcoholic solution. The reaction product is precipitated after a short time:

$$C_6H_2(CH_2Br)_2(CO_2 \cdot C_2H_5)_2 + 4NH_3 = C_6H_2(C_2H_2ON)_2 + 2C_2H_5OH + 2NH_4Br\downarrow$$

Mixing an alcoholic aniline solution with the solution of dibrominated cumidinic esters, the corresponding dianiles are obtained.

3. Dialdehydodicarboxylic Acids

These acids are prepared in two different manners:

Heating the dinitriles of tetrabromocumidinic acids in conc. sulfuric acid at 160°C until no more bromohydric acid is liberated and then pouring into water:

$$C_6H_2(CHBr_2)_2(CN)_2 + 6H_2O = C_6H_2(CHO)_2(CO_2H)_2 + 2NH_4Br + 2HBr.$$

Heating the bromides of tetrabrominated cumidinic acids in an aqueous suspension of calcium carbonate (Davies and Perkin analogy, loc. cit.):

$$C_6H_2(CHBr_2)_2(COBr)_2 + 4CO_3Ca = C_6H_2(CHO)_2(CO_2)_2Ca + 3CaBr_2 + 4CO_2.$$

a) 2,5-dicyano-1,4-bis(bromomethyl)benzene (V).
$C_6H_2(CH_2Br)_2(1,4)(CN)_2(2,5)$

A stream of bromine** is passed into 5 gm of molten β-cumidinic acid dinitrile (M.P. 209.5 - 210°C). The temperature is gradually decreased without letting the mass solidify, maintaining it then at 175°C. As soon as the increase in weight is about 5 gm (process duration 7 - 8 hrs), the product is absorbed in hot benzene, filtered, and a portion of the benzene is distilled. On cooling, a mixture of di- and tetrabrominated products is crystallized out. This is heated in boiling alcohol and filtered. The tetrabrominated product remains insoluble, while the dibrominated product crystallizes out on cooling. The yield is 7 - 8 gm.

The 2,5-dicyano-1,4-bis(bromomethyl)benzene crystallizes in small rods melting at 163°C and relatively well soluble in alcohol, benzene, and acetic acid. /551

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* This reaction was not described by Davies and Perkin.

** All experiments were made in a ground test tube with an ascending refrigerant; a stream of carbonic anhydride carried the bromine vapors.

For the analysis, the substance was dried* at 100°C:

0.1533 gm substance yielded 0.2169 gm CO_2 and 0.0308 gm H_2O
0.1705 gm substance yielded 14.6 cc N_2 (20°C, 696 mm)
0.1202 gm substance yielded 0.1422 gm AgBr
Calculated for $C_{10}H_6N_2Br_2$: C 38.23 H 1.93 N 8.92 Br 50.80%
Found: C 38.60 H 2.25 N 9.08 Br 50.34%.

b) 2,5-dicyano-1,4-bis(dibromomethyl)benzene (VI).
$C_6H_2(CHBr_2)_2(1,4)(CN)_2(2,5)$

This product, which is contained in a small quantity in the preceding preparation, can be obtained as main product by continuing the introduction of bromine until the theoretical amount of halogen has been absorbed. The product is digested in benzene, filtered, and left to crystallize.

This product is soluble in benzene and in acetic acid but insoluble in alcohol; it melts at 221°C. The product is not changed by 70% boiling sulfuric acid but only by conc. sulfuric acid at 160°C, with which it yields the corresponding dialdehydodicarboxylic acid:

0.1562 gm substance yielded 0.1460 gm CO_2 and 0.0166 gm H_2O
0.1928 gm substance yielded 11 cc N_2 (20°C, 693 mm)
0.1360 gm substance yielded 0.2160 gm AgBr
Calculated for $C_{10}H_4N_2Br_4$: C 25.44 H 0.86 N 5.94 Br 67.77%
Found: C 25.44 H 1.19 N 6.07 Br 67.59%.

c) 4,6-dicyano-1,3-bis(bromomethyl)benzene.
$C_6H_2(CH_2Br)_2(1,3)(CN)_2(4,6)$

Five grams of α-cumidinic acid dinitrile (M.P. 144 - 145°C) are brominated at a temperature of 165°C until a weight increase of 5 gm is reached. The mixture is absorbed in boiling benzene, filtered, and evaporated to a small volume. After allowing to stand for a long time, the product crystallizes in long prisms which effloresce in air, a process taking place more rapidly at 90°C, and melt at 114°C. The substance is highly soluble in benzene and alcohol and less soluble in ligroin:

0.1696 gm substance yielded 0.2371 gm CO_2 and 0.0370 gm H_2O
0.1710 gm substance yielded 14.8 cc N_2 (19°C, 694 mm)
0.1373 gm substance yielded 0.1645 gm AgBr
Calculated for $C_{10}H_6N_2Br_2$: C 38.23 H 1.93 N 8.92 Br 50.80%
Found: C 38.14 H 2.34 N 9.14 Br 50.98%.

Note. All brominated nitriles attack the skin and cause eczemas, requiring

* It is suggested to dry all products described in this paper on the water bath; they seem to crystallize with molecules of the solvent which they lose during the drying process.

careful handling.

d) Dibromide of 1,4-bis(bromomethyl)benzene-2,5-dicarboxylic acid. /552
$C_6H_2(CH_2Br)_2(COBr)_2$

Five grams of β-cumidinic acid are heated with 11 gm phosphorus pentachloride and 15 cc benzene until no more hydrochloric acid is liberated. The benzene and phosphorus oxychloride are distilled under vacuum, digested in benzene, filtered from possible impurities, and again distilled in vacuum.

The resultant chloride (M.P. 116°C) is treated with bromine as in the above examples, at a temperature not exceeding 160°C. As soon as the weight increase reaches 5 gm, i.e., slightly less than required by theory, the product is dissolved in a small amount of boiling benzene, filtered, and left to cool. The product crystallizes in long prisms that effloresce at 90°C and melt at 117 - 117.5°C. The product is sufficiently stable for being stored over prolonged periods of time under exclusion of humidity:

0.193 gm substance yielded 0.2103 gm CO_2 and 0.0258 gm H_2O
0.1309 gm substance yielded 0.2072 gm AgBr
Calculated for $C_{10}H_8O_2Br_4$: C 25.13 H 1.27 Br 66.92%
Found: C 24.97 H 1.37 Br 67.35%.

e) 1,4-bis(bromomethyl)benzene-2,5-dicarboxylic acid.

One gram of dibromide is heated in 8 gm formic anhydride close to 85 - 90°C. Carbonic acid and bromohydric acid will liberate. The reaction is terminated within a few minutes. The product is cooled, filtered, washed in water, and then washed in a small amount of boiling benzene.

The acid is insoluble in water, ether, and benzene but soluble in alcohol and glacial acetic acid. In these solvents, the acid crystallizes after a long period of rest in the form of brilliant flakes that decompose without melting at 339 - 340°C.

The product dissolves at room temperature in sodium carbonate; after a few minutes, the solution becomes turbid and p-pyromellitide precipitates quantitatively (see p.5):

0.1268 gm substance yielded 0.1340 gm AgBr
Calculated for $C_{10}H_8O_4Br_2$: Br 45.42%
Found: Br 44.99%.

The diethyl ether of this acid is prepared by pouring a small amount of absolute alcohol on the bromide. The mixture heats spontaneously, liberating bromohydric acid; the crystals change shape. The ether is purified by crystallization in alcohol in which it is little soluble. The product melts at 163 - 163.5°C under decomposition, yielding p-pyromellitide in theoretical quantity, under liberation of ethyl bromide:

0.1802 gm substance yielded 0.2743 gm CO_2 and 0.0636 gm H_2O
0.1228 gm substance yielded 0.1128 gm AgBr
Calculated for $C_{14}H_{16}O_4Br_2$: C 41.20 H 3.94 Br 39.10%
Found: C 41.45 H 3.99 Br 39.09%.

f) Dibromide of 1,4-bis(dibromomethyl)benzene-2,5-dicarboxylic acid. $C_6H_2(CHBr_2)_2(COBr)_2$

If, in the above example d), bromine is furthermore introduced at a temperature of 180 - 190°C until the weight increase reaches 11.5 gm, this new product /553 will be obtained. The product is extracted several times in hot benzene, with the tetrabrominated dibromide crystallizing on cooling and melting at 147°C. The product is relatively stable, but its boiling solution in benzene still liberates bromohydric acid; in addition, it is not recommended to repeat the crystallizations since this will in no way improve the purity of the derived product:

0.1233 gm substance yielded 0.2195 gm AgBr
Calculated for $C_{10}H_4O_2Br_6$: Br 75.45%
Found: Br 75.76%.

g) 1,4-bis(dibromomethyl)benzene-2,5-dicarboxylic acid.

This acid is prepared by reacting, at 85 - 90°C, anhydrous formic acid with the corresponding dibromide. The product is little soluble in water, acetic acid, and benzene, but highly soluble in alcohol. It decomposes at 259 - 260°C. The product dissolves at room temperature in sodium carbonate; on addition of hydrochloric acid to this solution, a product different from the acid used will precipitate out:

0.1285 gm substance yielded 0.1100 gm CO_2 and 0.0168 gm H_2O
Calculated for $C_{10}H_6O_4Br_4$: C 23.55 H 1.19%
Found: C 23.36 H 1.46%.

The diethyl ether of this acid is prepared by treating the dibromide with absolute alcohol. This product crystallizes in the alcohol in colorless prisms melting at 142 - 142.5°C:

0.1578 gm substance yielded 0.1714 gm CO_2 and 0.0390 gm H_2O
0.1188 gm substance yielded 0.1588 gm AgBr
Calculated for $C_{14}H_{14}O_4Br_4$: C 29.64 H 2.49 Br 56.38%
Found: C 29.63 H 2.76 Br 56.80%.

h) Dibromide of 1,3-bis(dibromomethyl)benzene-4,6-dicarboxylic acid. $C_6H_2(CHBr_2)_2(1,3)(COBr)_2(4,6)$

As conventional, 7 gm cumidinic dichloride (M.P. 82°C) are brominated at 160°C until the weight does not increase further. The mass is taken up in hot benzene and left standing. The crystals, dried at 90°C melt at 104°C:

and the material left to crystallize. The product will then be pure and the yield will be satisfactory.

The p-pyromellitide can also be prepared by starting from dibrominated acid or ether (No.5).

Properties: p-pyromellitide is difficultly soluble in boiling acetic acid but more readily soluble in nitrobenzene. The product is insoluble in sodium carbonate and dissolves in caustic alkalies at elevated temperature. The material decomposes without melting at 338 - 339°C. By oxidation with alkaline permanganate, the product is converted into pyromellitic acid.

k) Dilactone of 1,3-bis(oxymethyl)benzene-4,6-dicarboxylic acid; m-pyromellitide (XII).

The preparations are the same as for p-pyromellitide, preferably by treating the corresponding dibrominated dinitrile or, instead, the total mass of bromination by 70% silfuric acid. After crystallization in 70% sulfuric acid, the product will be completely pure.

The m-pyromellitide forms colorless prisms which are fairly soluble in boiling glacial acetic acid. The product melts, under decomposition, at 277.5 - 278.5°C. /555

0.1604 gm substance yielded 0.3714 gm CO_2 and 0.0464 gm H_2O
Calculated for $C_{10}H_6O_4$: C 63.15 H 3.18%
Found: C 63.17 H 3.24%.

l) Dianhydride of 1,4-bis(aminomethyl)benzene-2,5-dicarboxylic acid (p-pyromellitic diimidine) (XIII).

One gram of diethyl ether of 1,4-bis(bromomethyl)benzene-2,5-dicarboxylic acid is dissolved in boiling absolute alcohol, after which a stream of dry gaseous ammonia is passed. The reaction product will settle out. After about 1 hr, the product is hot-filtered, washed in boiling alcohol, and boiled with a solution of caustic soda. The obtained diimidine is insoluble in all conventional solvents even in quinoline. The product is a white powder which does not yet melt at 350°C.

0.1300 gm substance yielded 13 cc N_2 (12°C, 704 mm)
Calculated for $C_{16}H_8O_2N_2$: N 14.89%
Found: N 14.40%.

The m-diimidine isomer (XIV) is prepared in the same manner and has the same properties and decomposes at 340 - 350°C.

m) Dianile of Pyromellitic Acid

This product is prepared by heating to boiling in a large excess of aniline,

0.1961 gm substance yielded 0.3488 gm AgBr
Calculated for $C_{10}H_4O_4Br_4$: Br 75.45%
Found: Br 75.69%.

i) 1,3-bis(dibromomethyl)benzene-4,6-dicarboxylic acid.

This acid is prepared by reacting anhydrous formic acid with its bromide. The product is readily soluble in alcohol and ether and difficultly soluble in water. The product melts under decomposition at 224 - 225°C.

The product prepared from pure bromide has not been purified for analysis.

0.1004 gm substance yielded 0.0862 gm CO_2 and 0.0118 gm H_2O
0.1049 gm substance yielded 0.1554 gm AgBr
Calculated for $C_{10}H_6O_4Br_4$: C 23.55 H 1.19 Br 62.7%
Found: C 23.47 H 1.35 Br 63.0%

The diethyl ether of this acid is prepared by reacting absolute alcohol /554 with dibromide. This is readily soluble in organic solvents and may be crystallized in alcohol. The product melts at 93°C.

0.1404 gm substance yielded 0.1540 gm CO_2 and 0.0337 gm H_2O
0.1266 gm substance yielded 0.1666 gm AgBr
Calculated for $C_{14}H_{14}O_4Br_4$: C 29.64 H 2.49 Br 56.38%
Found: C 29.93 H 2.69 Br 56.11%.

j) Dilactone of 1,4-bis(oxymethyl)benzene-2,5-dicarboxylic acid, p-pyromellitide (XI).

One gram of 2,5-dicyano-1,4-bis(bromomethyl)benzene (1) is suspended in 30 cc 75% acetic acid. This acid is saturated by hydrogen chloride at room temperature, after which the tube is sealed and heated for 8 - 10 hrs at 180°C. The product is evaporated to dryness and taken up in water, after which the residue is dried and crystallized in nitrobenzene.

0.1285 gm substance yielded 0.2980 gm CO_2 and 0.0373 gm H_2O
Calculated for $C_{10}H_4O_4$: C 63.15 H 3.18%
Found: C 63.12 H 3.24%.

Second method: The mass obtained by bromination of the dinitrile of β-cumidinic acid (No.1) is heated with 15 - 20 times its weight of 70% boiling sulfuric acid, until no bromohydric acid is liberated. The product is hot-filtered on a silicate plate. The tetrabrominated nitrile remains insoluble. The 70% acid solution is diluted and the liquid of the whitish deposit is filtered. This product is heated with sodium carbonate and filtered; the pyromellitide remains insoluble. The product is dissolved in boiling caustic soda solution, filtered free of possible impurities and hot-precipitated from the alkaline solution by a mineral acid. This is dried in air, washed, and desiccated. The product still will contain impurities. To remove these, the material is hot-dissolved in 70% sulfuric acid, after which a few drops of water are added

1 gm of dibrominated ether used in the preceding example. The product is cooled, filtered, and washed in dilute hydrochloric acid. After crystallization in nitrobenzene, colorless flakes are formed which do not melt up to 360°C.

0.1382 gm substance yielded 10.8 cc N_2 (15°C, 702 mm)
Calculated for $C_{22}H_{16}O_2N_2$: N 8.23%
Found: N 8.55%.

n) 1,4-dialdehydobenzene-2,5-dicarboxylic acid (XV).
$C_6H_2(CHO)_2(1,4)(COOH)_2(2,5)$

A suspension of 2.7 gm dibromide of 1,4-bis(dibromomethyl)benzene-2,5-dicarboxylic acid (No.6) and 5 gm calcium carbonate in 100 cc water is heated to boiling. After 2 - 3 hrs, the mixture is cooled, acidulated, and left standing. The reaction product will settle gradually. The product is dried in air and crystallized in glacial acetic acid. The product melts at 257.5 - 258.5°C under decomposition. It has the properties of aldehydes.

0.1475 gm substance yielded 0.2938 gm CO_2 and 0.0373 gm H_2O
Calculated for $C_{10}H_6O_6$: C 54.05 H 2.72%
Found: C 54.30 H 2.83%.

Dioxime: A solution of aldehyde is heated in glacial acetic acid with an aqueous solution of hydroxylamine chlorohydrate, admixed with a small amount of sodium acetate. This forms a precipitate of colorless needles which are dried /556 in air. The product will decompose without melting at 153°C and is soluble in sodium carbonate at room temperature.

0.0722 gm substance yielded 6.75 cc N_2^0 ($22\frac{0}{2}$C, 713.8 mm)
Calculated for $C_{10}H_8O_6N_2$: N 10.0%
Found: N 10.06%.

If this reaction is allowed to proceed in alcohol instead of acetic acid, the same product is obtained, but no anhydride as in the case of phthalaldehydic acid.

Pyromellitic-bis(phenylazone): If a solution of aldehyde in acetic acid is mixed with a solution of phenylhydrazine in the same acid, the solution will turn yellow. If the product is heated slightly, a yellowish mass will precipitate out which, after crystallization in nitrobenzene, yields light-yellow flakes that melt at 352°C.

0.2356 gm substance yielded 33 cc N_2 (13°C, 695.2 mm)
Calculated for $C_{22}H_{14}O_2N_4$: N 15.3%
Found: N 15.1%.

o) 1,3-dialdehydobenzene-4,6-dicarboxylic acid (XVI).

This acid is prepared like its isomer (No.14), by starting from the corresponding dibrominated dibromide of the acid (No.8). The product melts at

246 - 247°C under decomposition and has properties analogous to those of its isomer.

0.1423 gm substance yielded 0.2822 gm CO_2 and 0.0382 gm H_2O
Calculated for $C_{10}H_8O_6$: C 54.05 H 2.72%
Found: C 54.1 H 3.00%

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Translated for the National Aeronautics and Space Administration by the O.W.Leibiger Research Laboratories, Inc.